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BAND ENERGY OF GOLD

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(*Received June* 9, 1966)

ABSTRACT. The band energy of gold has been calculated for the point of the Brillouin Zone by the Augmented Plane Wave (A.P.W.) method with the help of the universal potential given by Gaspar for the noble metals. The convergence was tested for the state Γ_1 and is seen to be quite rapid.

INTRODUCTION

The problem of finding the energy levels in a solid is essentially a manybody one the solution of which is practically impossible without the help of some approximation methods. In practice, one starts with one electron Schrodinger equation with a potential which is periodic with the period of the crystal lattice. The energy is then calculated by a proper choice of the one electron wave function which must satisfy the Block's condition

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_k(\vec{r})$$

where $\vec{k}$ is a vector of the momentum space and the function $u_{\vec{k}}(\vec{r})$ has the periodicity of the crystal lattice. There are various methods to find out the form of $u_k(r)$ of which the simplest one is to expand $u_{\vec{k}}(\vec{r})$ in terms of plane waves whose wave vectors are the reciprocal lattice vectors. But this method has the disadvantage that the lowest value of the secular equation may converge to the lowest eigen value of the atomic states thus necessitating large number of terms in the expansion. This difficulty has been overcome by Herring (1940) in his Orthogonalized Plane Wave (O.P.W.) method by orthogonalizing the plane waves with atomic core states. Although this method has become very successful in the case of simple metals and semi conductors, its success depends on the accurate knowledge of the atomic eigen values and eigen functions in advance. Another serious difficulty of this method is that for some symmetry states the opw's may be automatically orthogonal to the core states and hence the convergence will be poor. This point has been discussed by Hermann (1954) who suggests that in order to improve the convergence, one must add some function to the opw's which will be rapidly varying near the nucleus of the atoms forming the solid. But in the present formalism of the O.P.W. method, there is not much scope in adding rapidly varying functions near the nucleus.

There is yet another method, the Augmented Plane Wave Method, which takes into account many of the above discrepancies. In fact Slater (1964) has pointed out that the Augmented Plane Wave method is a direct answer to Herman's problem of addition of rapidly varying function near the nucleus. Another disadvantage of the O.P.W. method is that it requires the accurate knowledge of eigenvalues and eigen functions in addition to the knowledge of the potential. That is why the O.P.W. method has not been tried in case of heavier metals such as gold because of the nonavailability of Hartree-Fock solution of the atomic states.

The Augmented Plane Wave method was originally proposed by Slater (1937) and later modified by Slater and Saffren (1953). Since then there have been many applications of the method by various authors. Among them the most notable ones are Howarth (1955) and Burdick (1963). Both of them have applied the method to copper with different potentials but very little has been attempted in the case of the other two noble metals e.g. silver and gold. Since there is already one calculation on silver by the O.P.W. method (Chatterjee and Sen, 1966), we have attempted in this paper to calculate the energy bands in gold by the Augmented Plane Wave Method.

OUTLINE OF THE METOD

The augmented plane wave method has been originally proposed by Slater (1937) and later modified by Slater Saffren and (1953), and successfully applied to copper by Howarth (1955). Following these authors each augmented plane wave may be written as

$$\phi_{\vec{k}} = a_0 \left[\epsilon(r-r_0) e^{i\vec{k}\cdot\vec{r}} + \epsilon(r_i-r) \sum_{l,m} 4\pi i^l \frac{j_l(kr_i)}{R_l(E,r_i)} Y_{lm}^*(\theta_k, \phi_k) Y_{lm}(\theta, \phi) R_l(E, r) \right] \tag{1}$$

where ϵ is a step function

$$\epsilon(x) = 1 \quad \text{for} \quad x \geqslant 0$$

$$\epsilon(x) = 0 \quad \text{for} \quad x < 0$$

Here $\vec{k}$ is the reduced wave vector, r_i is the radius of the inscribed sphere on which the plane wave are joined with the spherical waves and $R_l(E, r)$ is the solution of the radial equation.

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR_l}{dr} \right) + \left[E - V(r) - \frac{l(l+1)}{r^2} \right] R_l = 0 \tag{2}$$

with the energy E which is the expectation energy of the augmented planes wave. Thus, in the construction of each augmented plane wave one computes the radial

wave functions $R_l(E, r)$ for a number of energies and l and then finds out the correct value of E and $R_l(E, r)$ from the following equation where ω is the volume of the unit cell outside the inscribed sphere.

$$(E-k^2)\omega = 4\pi r_i^2 \sum_l (2l+1) j_l^2(kr_i) \left[\frac{d}{dr} \ln R_l(E, r) \right]_{r=r_i} \quad \ldots (3)$$

Equation (3) is the condition for the expectation energy. The equation is satisfied by means of trial and is quite laborious. But once the augmented plane waves are constructed accurately the problem becomes quite easy. One then utilises the variational procedure based on the linear combination of $\phi_k s$ to obtain the secular equation. The matrix elements of the secular equation are given by

$$< k_1/k_2 > = \omega \delta k_1 k_2 - 4\pi r_i^2 \left\{ \frac{(j_1 | \vec{k}_1 - \vec{k}_2 | r_i)}{| \vec{k}_1 - \vec{k}_2 |} (1-\delta k_1 k_2) \right\}$$

$$- \sum_l (2l+1) j_l(k_1 r_i) j_l(k_2 r_i) P_l(\cos \theta_{k_1 k_2}) I_l \quad \ldots (4a)$$

where $I_l = \left[\frac{d}{dr} \ln R_l(E_2, r_i) - \frac{d}{dr} \ln R_l(E_1, r_i) \right] [E_1 - E_2]^{-1}$ for $E_1 \neq E_2$

$$= - \frac{d}{dE} \left[\frac{d}{dr} \ln R_l(E, r) \right]_{r=r_i} \quad \text{for} \quad E_1 = E_2$$

and

$$< k_1 | \mathrm{H} | k_2 > = \vec{k}_1 . \vec{k}_2 \left[\omega \delta k_1 k_2 - 4\pi r_i^2 j_l \left(\frac{| \vec{k}_1 - \vec{k}_2 | r_i)}{| \vec{k}_1 - \vec{k}_2 |} (1-\delta k_1 k_2) \right] \right.$$

$$+ 4\pi r_i^2 \sum (2l+1) j_l(k_1 r_i) j_l(k_2 r_i) P_l(\cos \theta_{k_1 k_2}) J_l \quad (5)$$

where

$$J_l = \left[E_1 \frac{d}{dr} \ln R_l(E_2 r) - E_2 \frac{d}{dr} \ln R_l(E_1 r) \right]_{r=r_i} (E_1 - E_2)^{-1} \quad \text{for} \quad E_1 \neq E_2$$

$$= -E \frac{d}{dE} \left[\frac{d}{dr} \ln R_l(E, r) \right]_{r=r_i} + \left[\frac{d}{dr} \ln R_l(E, r) \right]_{r=r_i} \text{for } E_1 = E_2$$

RESULTS AND DISCUSSION

In the present calculation on gold, the radial equation (2) is solved numerically by means of the Numerov method (Pratt, 1952) with the universal potential given

by Gaspar (1953). Since at present we are concerned with the power of convergence of the method, we have taken nine augmented plane waves for the point Γ of the Brillonin zone corresponding to the wave vectors (000) and (111). We have solved the radial wave equation (2) for $l = 0$ to $l = 6$. For $l > 6$ the contribution to the right hand side of equation (3) become negligible. The value of $\left[\frac{dr}{dr} ln\, R_l(E, r)\right]_{r=r_i}$ are given for the augmented plane wave with the reduced wave vector (111).

TABLE I

Energy E	l	$\left[\frac{d}{dr} ln R_l\right]_{r=r_i}$	$\frac{d}{dE}\left[\frac{d}{dr} ln R_l\right]_{r=r_i}$
−.85 ryd.	0	−0.25659	−0.93825
	0	−9.91597	−38.50300
	1	− 1.82468	− 0.24450
	2	+ 0.09992	− 0.71450
1 ryd.	3	− 0.09391	− 0.89400
	4	− 0.77379	− 0.36050
	5	+ 1.31446	+ 0.19900
	6	+ 1.28000	− 0.22800

The nine by nine secular determinant has been factorised by the group theoretical consideration to give the states Γ_1, Γ_{15}, Γ_{25}' and Γ_2' of which the determinant for Γ_1 is two by two and all the other states are one by one. The values are given in Table II from which the convergence for the state Γ_1 can be seen to be quite rapid.

TABLE II

Value of the energy in ryd

States	1st order	2nd order
Γ_1	− .84908	− .85004
Γ_{15}	.76034	
Γ'_{25}	1.34997	
$\Gamma_{2'}$	1.48467	

The calculation for the other symmetry points L and X and for the higher waves for the point is under progress.

ACKNOWLEDGMENTS

The authors are grateful to Prof B. N. Srivastava for his keen interest in the problem. Authors are also grateful to C.S.I.R. for financial assistance.

REFERENCES

Burdick, G. A., 1963, *Phys. Rev.*, **129**, 138.
Chatterjee, S, and Sen, S. K., 1966, *Proc. Phys. Soc.*, **87**,
Gàspar, R., 1953, *Acta Phys. Acad. Sc. Hung.*, **3**, 263.
Herman, F., 1954, *Phys. Rev.*, **93**, 1214.
Herring, C, 1940, *Phys. Rev.*, **57**, 1169.
Howarth, D. J., 1955, *Phys. Rev.*, **99**, 469.
Pratt, G. W., 1952, *Phys. Rev.*, **88**, 1217.
Saffren, M. M., and Slater, J. C., 1953, *Phys. Rev.*, **92**, 1126.
Slater, J. C., 1937, *Phys. Rev.*, **51**, 486.
——— 1964, *Adv. Qnt. Chem.*, **35**, 1964.